PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Perfluorocarbon Polymer Coating Compositions

We, E.I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to coating compositions and to articles coated therewith. More particularly, this invention relates to modified aqueous dispersion coating compositions having a combination of a perfluorocarbon polymer and a heat-convertible organopolysiloxane resin as the essential organic film-forming materials.

Tetrafluoroethylene polymers characterized by superior heat and chemical resistance have found extensive use as speciality coatings where these properties are particularly important. Another important characteristic of the perfluorocarbon polymer is the release properties, i.e. anti-adhesion or low order of adhesion between the perfluorocarbon polymer and another film-forming material ordinarily adhesive in contact therewith. This property has lead to extensive use of coatings formulated with the perfluorocarbon polymer as anti-stick or release coatings for die molds, extrusion dies, cookie tins, bread pans, and, more recently, non-stick fry pans and other anti-stick cooking utensils.

The aforementioned advantageous characteristics of the perfluorocarbon polymers present significant application problems. Because of the chemical inertness, the perfluorocarbon polymers cannot be ordinarily applied in solution form for lack of an adequate solvent for the polymer. A convenient method for applying the perfluorocarbon polymer as a coating is in the form of an aqueous suspensoid of colloidal particles thereof. Such an aqueous dispersion is applied to a heat-resistant substrate, the applied coating is dried by volatile loss of water and other ordinarily volatile components of the liquid composition, and the resulting dry coating which ordinarily lacks adequate continuity is heated at an elevated temperature to fuse the deposited particles of the perfluorocarbon polymer.

The heat resistance of the perfluorocarbon polymer necessitates a high baking temperature to accomplish fusion of the colloidal particles to a continuous film. With tetrafluoroethylene polymer, baking temperatures are ordinarily in the range of 675°F to 775°F. With interpolymers of hexafluoropropylene and tetrafluoroethylene, such as defined in Specification No. 829,600, somewhat lower baking temperatures can be used, e.g., temperatures ordinarily in the range of 550°F to 650°F.

Unless the substrate to be coated initially has surface irregularities to promote mechanical anchorage of the perfluorocarbon polymer coating, the substrate is treated either chemically to etch the surface or mechanical anchorage of the coating in compensation for the anti-stick properties of the coating. While anti-adhesion is a desirable characteristic for many purposes, it is a disadvantage for many other potential uses for the perfluorocarbon polymer coating. With composite finishing systems in which the perfluorocarbon polymer coating is the undercoat and another organic coating

is applied thereover, the anti-adhesion characteristics of the perfluorocarbon polymer inhibits adequate intercoat anchorage. For example, with electrical assemblies fabricated with wire electrically insulated with a layer of perfluorocarbon polymer, anti-adhesion and lubricity of the insulation present serious handling problems, and it is highly desirable to impregnate or encapsulate the electrical assembly with an insulating varnish or encapsulating composition which adheres to the perfluorocarbon insulation and provides rigidity to the assembly.

Another characteristic of the perfluorocarbon polymers which is disadvantageous to many uses is softness which permits it to be easily abraded or cut through in handling.

A further characteristic which is disadvantageous is the necessity of applying the coating at a relatively thin dry coating weight, e.g., at a fractional mil coating thickness, and applying a plurality of coats to obtain the desirable useful thickness. Primers having perfluorocarbon polymer as the essential organic film-forming material ordinarily are applied satisfactorily at dry film thickness up to about 6.0 mil per coat. Topcoats are ordinarily applied adequately at about 0.5 mil to about 2 mils per coat.

We have found that one or more of the aforementioned disadvantages associated with the use of the perfluorocarbon polymer as a coating material are overcome by suitable modification of the aqueous suspensoid of the perfluorocarbon polymer with a heat-convertible organopolysiloxane resin and chromic acid, and, if desired, an inorganic polybasic oxy-acid of phosphorus or sulphur.

The present invention accordingly comprises a water-dilutable aqueous dispersion coating composition consisting essentially of:—

(A) colloid particles of at least one perfluorocarbon polymer, said polymer being tetrafluoroethylene polymer or hexafluoropropylene/tetrafluoroethylene interpolymer, dispersed in an aqueous continuous phase,

(B) a solution of a heat convertible (as herein defined) organo-polysiloxane resin containing structural units of the formula:

$$\begin{array}{c} R \\ | \\ -Si-O- \\ | \\ R' \end{array}$$

in which R and R′, which may be the same or different (and which may vary from one structural unit to another), are monovalent hydrocarbon radicals in a water-immiscible organic solvent therefore as a dispersed phase,

(C) a sufficient quantity of one or more water-soluble anionic surfactants to maintain the stability of the dispersion of the perfluorocarbon polymer and the solution of organo-polysiloxane in the continuous aqueous phase, and

(D) chromic acid.

Pigment may be present in the coating composition in proportions up to 500 parts by weight per 100 parts total weight of the perfluorocarbon polymer and the organo-polysiloxane resin.

In the following description, reference is made to the polybasic oxy-acid component and it is to be understood that this essentially comprises chromic acid and may, if desired, additionally include an oxy-acid of phosphorus or sulphur.

Useful proportions of the organopolysiloxane resin are in the range of from 3 parts to 100 parts per 100 parts by weight of the perfluorocarbon polymer, preferably 10-35 parts of the organopolysiloxane resin.

Useful proportions of the polybasic inorganic oxy-acid are in the range of from 5 parts to 200 parts by weight, including at least 5 parts of chromic acid, per 100 parts total weight of the perfluorocarbon polymer and the organopolysiloxane resin. However, no significant advantage is seen in using more than 100 parts of the oxy-acids on the indicated basis. Preferred proportions of the oxy-acid are in the range of 20 to 65 parts on the indicated basis. The oxy-acid components can be solely chromic acid or oxy-acid mixtures of chromic acid and another of the identified inorganic oxy-acids, which mixture provides at least 5 parts of chromic acid per 100 parts of the perfluorocarbon polymer and the organopolysiloxane resin. Preferably the oxy-acid mixtures contain at least 10 parts of chromic acid per 100 parts by weight of the acid mixture, the mixture being preferably composed of chromic acid and orthophosphoric acid. The orthophosphoric acid is preferably in the proportion of 50 to 150 parts per 100 parts by weight of chromic acid.

The total proportion of surfactant component, including surfactant introduced to stabilize the aqueous suspensoid of the perfluorocarbon polymer, surfactant introduced to emulsify or disperse the solution of the organopolysiloxane in the continuous aqueous phase, and surfactant introduced to facilitate dispersing the pigment, ordinarily is at least 3 parts and ordinarily does not exceed 50 parts per 100 parts by weight of the perfluorocarbon polymer. Presence of an anionic surfactant is preferred and it is ordinarily present in the proportion of at least 2 parts per 100 parts of the perfluorocarbon polymer, preferably in the range of 5 to 20 parts. A non-ionic surfactant may be present in combination with the anionic surfactant in proportions up to above 40 parts, preferably 5 to 30 parts per 100 parts of the perfluorocarbon polymer. Presence

of the non-ionic surfactant provides the aqueous dispersion with an advantageous increase in body.

Aqueous suspensoids of tetrafluoroethylene polymer useful in this invention are described, for example, in Specification No. 631,570. Concentrated aqueous suspensoids of colloidal particles of tetrafluoroethylene polymer, such as described in Specification No. 631,504, are especially useful as raw materials preparing the coating compositions of this invention. Such aqueous suspensoids are commercially available and ordinarily contain a surfactant, e.g., anionic sodium lauryl sulfate or non-ionic "Triton" X-100 (trade mark) in the proportion of about 2 to 6 parts per 100 parts of the perfluorocarbon polymer as a stabilizer for the suspensoid. Interpolymers of hexafluoropropylene and tetrafluoroethylene useful in the preparation of the coating compositions of this invention are described in Specification No. 829,600. Aqueous suspensoids of these interpolymers are commercially available and ordinarily contain a non-ionic surfactant, e.g., "Triton" X-100 octylphenoxypolyethanoxyethanol in the proportion of about 3 to 6 parts per 100 parts by weight of the perfluorocarbon interpolymer. Commercially available aqueous suspensoids of these perfluorocarbon polymers ordinarily contain up to about 60% by weight of the polymer.

When mixtures of the perfluorocarbon polymers are used, ordinarily at least 5 parts of the tetrafluoroethylene polymer and at least 10 parts of the interpolymer are necessary for an effective contribution per 100 parts of the perfluorocarbon polymer mixture.

The heat-convertible organopolysiloxane resin, the second essential component of the coating composition is organic-solvent-soluble in the non-converted state and is water-dispersible. The expression "heat-convertible" is used herein in relation to the organopolysiloxane resin, to refer to such resins which, when deposited as a thin coat on a heat-resistant substrate and heated at temperatures in the range of about 210°F to about 750°F, yield smooth continuous films which are substantially insoluble in solvents contained in the starting solution of the organopolysiloxane resin. Useful organopolysiloxane resins contain structural units of the formula:

$$\begin{array}{c} R \\ | \\ -Si-O- \\ | \\ R' \end{array}$$

wherein R— and R'— represent monovalent hydrocarbon radicals; the polysiloxane may be, and preferably is, made of up of a combination of a number of structural units of this formula which have different R and R' substituents. The R and R' substituents are usually a combination of alkyl and aryl radicals with methyl-phenylpolysiloxanes being preferred; the preferred polysiloxane resins contain the methyl and phenyl radicals in the proportion of from 1 to 2 per silicon atom in the siloxane molecule. It is also preferred that the methylphenylpolysiloxane resins should contain from 0.5 to 2 methyl substituents per phenyl substituent. Useful organopolysiloxane resins and the process for their preparation are described in U.S. Patent 2,258,222. Organopolysiloxane resins useful in formulating the coating compositions of this invention are commercially available under the following designations: (Dow Corning) DC-801, DC-803, DC-805, DC-806, and DC-840 silicone resins; (General Electric) SR-82, SR-112, SR-02, SF-69 and Silicone Resin 81727; and (Union Carbide and Carbon) Silicone Resins R-62 and R-64.

As indicated hereinbefore, the proportion of organopolysiloxane resin can range up to 100 parts per 100 parts by weight of the perfluorocarbon polymer, at least 3 parts of organopolysiloxane being required to provide an effective contribution. The preferred proportion is 10 to 35 parts, and while higher proportions up to 100 parts provide useful compositions, they do not usually have the desired balance of properties. In this range of higher proportions of the organopolysiloxane resin, the resulting coating lacks the desired toughness.

The organopolysiloxane resin is ordinarily used in the form of a solution of the resin in a volatile liquid water-immiscible organic solvent for the organopolysiloxane resin. Any organic solvent which is ordinarily used in paint, varnish and lacquer formulations which is a solvent for the organopolysiloxane resin and which is characterized by water-immiscibility to provide dispersibility in water can be used to prepare the solution of the organopolysiloxane resin. Such solvents can be hydrocarbons, esters, ketones, ethers, and mixtures thereof. Hydrocarbons are preferred solvents, e.g., toluol, xylol, benzene, high solvency petroleum naphthas, mineral spirits, hexane, cyclohexane, and the like. The solution of the resin can have a content of up to about 75% by weight of the organopolysiloxane resin, the resin concentration ordinarily being in the range of 20 to 60% by weight of the solution. Useful solutions of the resin can have a resin concentration of 10% or even lower when it is desirable to increase the proportion of solvent dispersed in the continuous aqueous phase. Ordinarily the organic solvent does not exceed a proportion of about 40% based on the total weight of the coating composition. Preferred proportions are in the range of 5% to 25%. Use

of a high proportion of solvent reflects a reduction in the content of the film-forming components of the coating composition which in turn ordinarily reflects a reduction in the coating weight per coat.

The third essential component of the aqueous dispersion coating composition is the water-soluble surfactant which includes an anionic surfactant. The useful proportions of the surfactant are recited hereinbefore. Sodium alkyl sulfates having 10 to 18 carbon atoms in the alkyl substituent are representative for stabilizing the aqueous suspensoid of the perfluorocarbon resin, sodium lauryl and sulfate being especially useful. While the aqueous suspensoid of the perfluorocarbon resin may supply a substantial proportion of the anionic surfactant, the content thereof can be supplemented with additional surfactant which may be anionic or non-ionic. Preferably the supplemental surfactant is a combination of anionic and non-ionic surfactants. The anionic surfactant can be a sodium alkyl sulfate or an alkyl surfonate salt, each having 10 to 18 carbon atoms in the alkyl substitutent, or an alkyl-arylsulfonate, e.g., a dialkylanphthalene sulfonate having 3 or 4 carbon atoms in each alkyl substituent. Sodium sulfonates of a plurality of naphthene units condensed with formaldehyde are particularly useful as the anionic surfactant for dispersing the pigment in an aqueous medium. Non-ionic surfactants, e.g., "Triton" X-100 octylphenoxypolyethanoxyethanol, are ordinarily preferred in dispersing the pigment in a non-aqueous medium.

Useful non-ionic surfactants which can be included in combination with the anionic surfactants are represented by polyethanoxyethers of alkyl phenols, alcohols or mercaptans, and polyethanoxy esters of hydrophonbic fatty acids and polypropylene ether esters of such fatty acids. Preferred non-ionic species are alkylphenoxypolyethanoxyethanols having 7 to 12 carbon atoms in the alkyl substituent and having from 8 to 15 moles of ethylene oxide condensed per mole of alkylphenol.

The fourth essential component of the coating composition is chromic acid, or a mixture of chromic acid with at least one polybasic oxy-acid of phosphorous or sulfur, such acid mixtures preferably including the tribasic orthophosphoric acid in combination with chromic acid. For calculating purposes, chromic acid as referred to throughout the specification and claims is identified as CrO_3 which in the aqueous medium yields chromic acid. Typical polybasic acids which can be used in combination with the chromic acid include orthophosphoric, pyrophosphoric, sulfuric and sulfurous acids. These polybasic acids enhance the curing of the organopolysiloxane resin and in crosslinking the polysiloxane resin, at least a portion of the oxy-acid, especially orthophosphoric and chromic acids, apparently reacts with the polysiloxane resin to become an integral part of the resulting crosslinked resin. While chromic acid can be used as the sole polybasic oxy-acid component, a mixture of chromic acid and the tribasic orthophosphoric acid is preferred. As stated hereinbefore, the proportion of oxy-acid preferably is in the range of 20 to 65 parts per 100 parts total weight of the perfluorocarbon polymer and the organopolysiloxane resin.

Pigments and extenders can be present in the coating composition in proportions up to 500 parts per 100 parts total weight of the perfluorocarbon polymer and the organopolysiloxane resin. Useful pigments and extenders are necessarily substantially non-reactive with the oxy-acid component of the composition. Metal oxides, chromates, silicates, sulfates, phosphates, carbon black, colloidal silica and montmorillonite clays are typical materials useful for pigmentation. Metal hydroxide and metal carbonate pigments can be used at low acid concentrations where moderate reactivity of the pigment can be tolerated.

Preferred proportions of total pigment range from 10 parts to 150 parts per 100 parts total weight of the perfluorocarbon resin and the organopolysiloxane resin. Within the range of up to 50 parts of total pigment, the finished deposited from the coating composition and cured exhibits advantageous retention of properties ordinarily attributed to the presence of the perfluorocarbon resin and further exhibits improved hardness, improved film-build, improved abrasion resistance and improved adhesion. When the pigmentation is in the range above 50 parts, the contribution of the perfluorocarbon polymer to the film properties are proportionately decreased with increasing proportions of pigmentation, but this increase in pigmentation in combination with the oxy-acid cured organopolysiloxane resin reflects further improvement in film-build, hardness, abrasion resistance, and adhesion. These more highly pigmented compositions are advantageously bondable with other organic coatings which ordinarily do not adhere adequately to tetrafluorocarbon polymer and hexafluoropropylene-tetrafluoroethylene interpolymer substrates.

Still other modifiers in addition to the aforementioned essential components may be present in the coating composition, but their presence is not essential to accomplishment of the objectives of this invention. Bodying agents, e.g., methyl cellulos, dimethyl, dioctyl ammonium bentonite clay, high molecular weight carboxylic vinyl polymers; flow control agents; and other additives can be included in ordinary small pro-

portions necessary to accomplish their purpose.

Coating compositions of this invention are applicable at concentrations ranging up to 70% by weight of solids, including the oxy-acid component as part of the solids content which is deposited from the composition as a finish. The coatings are usually applied at a solids content of at least 20% by weight, preferably at 30% to 60% by weight. However, for some purposes, application at 10% or even as low as 5% by weight is considered to be practical. Inasmuch as the compositions have a continuous aqueous phase and are water-dilutable, water is used to thin high solids compositions to lower concentrations of solids.

The coating compositions of this invention are prepared by blending a preformed solution of the organopolysiloxane resin in a water-immiscible solvent with an aqueous suspensoid of the perfluorocarbon resin in the presence of a water-soluble surfactant including an anionic species to thereby form a dispersion having a continuous aqueous phase and the solution of the organopolysiloxane resin as a dispersed phase, and thereafter blending the inorganic polybasic oxy-acid component with the resulting aqueous dispersion. Preferably, the solution of the organopolysiloxane resin is predispersed in water in the presence of a water-soluble surfactant and the resulting aqueous dispersion is blended with the aqueous suspensoid of the perfluorocarbon resin. Blending can be by an ordinary means, but high speed mixing and heavy duty mixing usually is avoided because of adverse effects on the stability of the aqueous suspensoid of the perfluorocarbon polymer.

When the composition is pigmented, the pigment is initially dispersed in either an aqueous medium or non-aqueous liquid medium in the presence of a surfactant to facilitate wetting of the pigment. The resulting pigment dispersion is blended with the aqueous dispersion of the solution of the organopolysiloxane resin and the aqueous suspensoid of the perfluorocarbon polymer. Preferably, the pigment is predispersed in a non-aqueous liquid medium comprising essentially a soluble surfactant and a solution of the organopolysiloxane resin in a water-immiscible organic solvent therefor. However, water and the soluble surfactant alone or an aqueous dispersion of the organic solution of the organopolysiloxane resin can be used as the initial dispersion medium for the pigment.

Minimum mechanical working of the aqueous suspensoid of the perfluorocarbon resin is desired for stability reasons and consequently, the pigment preferably is not initially dispersed in the presence of the aqueous suspensoid of the perfluorocarbon resin. The preformed aqueous pigment dispersion is merely blended with the aqueous suspensoid.

Ancillary components can be included in either the aqueous suspensoid of the perfluorocarbon polymer, the aqueous dispersion of the solution of the organopolysiloxane resin, the preformed pigment dispersion, or any combination of these three, according to the ordinary techniques of adding these components. Ordinarily, these ancillary components are modifiers for the aqueous suspensoid of the perfluorocarbon polymer and are added directly thereto or to any combination which includes the suspensoid.

As indicated hereinbefore, two main categories of compositions evolve from this invention, i.e., those having high retention of the perfluorocarbon polymer characteristics with significant improvements and those in which the improvements predominate with the contribution of the perfluorocarbon polymer being of less importance. An important consideration of the compositions of this invention is that high temperature baking or even heating to fusion temperature of the perfluorocarbon polymer is not necessary to the deposition of useful finishes. The deposited coating will cure by simply air-drying at ambient temperature, e.g., the coatings dry tack-free in one hour at 77°F. Moderate force drying temperatures can be used, e.g., the coatings dry tack-free in 10 minutes at 180°F . In the absence of high temperature baking and the use of fusion temperatures, the resulting finishes do not develop optimum properties attributed to the characteristics of the perfluorocarbon polymer. Where these optimum properties are desired, baking temperatures in the range of 675°F to 775°F, preferably 5 to 25 minutes at 750°F, are used to cure compositions in which the perfluorocarbon polymer is tetrafluoroethylene polymer. Somewhat lower temperatures are used when the perfluorocarbon polymer is an interpolymer of hexafluoropropylene and tetrafluoroethylene or mixtures thereof with the tetrafluoroethylene polymer, e.g., baking temperatures in the range of 550°F to 650°F, preferably 5 to 25 minutes at 625°F.

In the absence of fusion of the colloidal particles of the perfluorocarbon polymer in the deposited finish, these particles exist in a film-forming matrix of the cured organopolysiloxane/oxy-acid combination substantially as perfluorocarbon colloidal pigment particles rather than as film-forming material. Such uncoalesced or unfused particles of perfluorocarbon polymer continue to contribute some of their advantageous characteristics to the properties of the finish. Intermediate baking temperatures such as from 250°F to 425°F ordinarily used com-

mercially for curing conventional baking finishes can be used in curing the finishes of this invention to enhance the cure of the organopolysiloxane resin and facilitate removal of surfactant, but such curing temperatures do not enhance the contribution of the perfluorocarbon polymer in the absence of fusion.

Coating compositions of this invention formulated with a high relative proportion of the perfluorocarbon polymer and low pigmentation or unpigmented, e.g., below about 50 parts of pigment per 100 parts total weight of the perfluorocarbon polymer and the organopolysiloxane resin are preferably cured at a temperature sufficient to fuse the colloidal particles of the perfluorocarbon polymer. With coating compositions of this invention formulated with the perfluorocarbon polymer moderately or highly modified with pigment and having substantial proportions of the organopolysiloxane resin as film-forming material, adequate curing is accomplished with ordinary moderate baking temperatures or even by air-drying at ambient temperatures. Baking of these compositions at higher temperatures sufficient to fuse the perfluorocarbon polymer particles does not significantly enhance the properties of the finish contributed by the perfluorocarbon polymer. Advantages of moderate baking over air-drying of the invention coatings reside in enhanced adhesion, hardness, and abrasion resistance and reduced water-sensitivity.

The coating compositions of this invention can be applied by any of the conventional coating techniques such as by spraying, brushing, dipping or roller coating. The coating compostiions can be applied to any of a wide variety of substrates. While the substrate is preferably heat-resistant, e.g., iron, steel, copper, bronze, brass, nickel, aluminum, tungsten, titanium and alloys of the indicated metals, glass and other ceramic materials, to accommodate fusion temperatures for the perfluorocarbon polymer, innumerable other less heat-resistant substrates, e.g., wood, paper, textiles, rubber synthetic elastomers and the like, can be coated with the invention compositions in consideration of curing the deposited coating composition at moderate baking temperatures or even at ambient temperatures such as 77°F. A limitation is that the substrate be tolerant of exposure to the aqueous composition containing the oxy-acid.

Compositions of this invention are applicable in substantially thick coats, e.g., up to about 5 mils dry thickness per coat. Such film thicknesses are significantly thicker than are applicable with conventional coatings formulated with aqueous suspensoids of the perfluorocarbon polymer or interpolymers. The relative increase in thickness is at least 50% greater, the increase ordinarily being 100% or more. These finishes cured at fusion temperature exhibit retention of the desirable properties attributed to the contribution of the fused perfluorocarbon polymer, i.e., heat, chemical, and electrical resistance and durability, when the coating composition is either a clear formulation or pigmented up to about 50 parts of pigment on the indicated basis. In addition, these cured finishes exhibit the advantageous improvements of significantly enhanced hardness, abrasion resistance and adhesion.

Baked finishes and air-dry finishes of the invention compositions in which the proportion of pigment is in the range of 50 to 500 parts, per 100 parts total weight of the perfluorocarbon polymer and the organopolysiolxane resin, exhibit the same advantageous improvements, but the contributive characteristics of the perfluorocarbon polymer are diminished with decreasing relative proportions of the perfluorocarbon polymer.

The complete liquid coating compositions are characterized by limited package stability, particularly when the proportoin of the oxy-acid component is high. Because of the potential instability, the coating composition is preferably packaged as a two-package combination having a stable aqueous solution of the oxy-acid component in one package and a stable aqueous dispersion constituting the balance of the composition in the second package. Appropriate proportions of the contents of the two packages are simply mixed together to complete the composition. If desired, the composition can be packaged with a greater plurality of component packages which are simply blended to complete the formulation, e.g., a three-package combination is feasible in which the aqueous oxy-acid is in one package, the stable aqueous suspensoid of the perfluorocarbon polymer in the second package, and the clear or pigmented aqueous dispersion of the solution of the organopolysiloxane resin in the third package. In combining the three packages, it is preferred to initially combine packages two and three and then blend in package one, although the acid can be blended separately with either package two or package three before the entire combination is combined.

The following examples are intended to illustrate this invention and not to limit it in any way. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

First Portion	*Parts by Weight*
Cr_2O_3 Chromium Oxide Pigment	31.8
TiO_2 Titanium Oxide Pigment	18.2
DC-801 Organopolysiloxane Resin Solution, 60% in Xylol	14.6

"Triton" X-100 Octoylphenoxy-polyethanoxyethanol	7.3
Xylol—Industrial 10°	54.0
Toluol	9.1
Second Portion	
Aqueous Sodium Lauryl Sulfate Solution, 23%	36.9
"Triton" X-100 Non-ionic Surfactant	20.0
Water	53.0
DC-801 Organopolysiloxane Resin Solution, 60% in Xylol	6.5
DC-803 Organopolysiloxane Resin Solution, 50% in Xylol	7.6
Third Portion	
Aqueous Suspensoid of Tetrafluoroethylene Polymer—60% Polymer and 3 Parts of Sodium Lauryl Sulfate per 100 Parts of the Polymer	142.0
Water	25.0
Fourth Portion	
Water	15.0
Chromic Acid CrO_3 99.5+%	13.5
Orthophosphoric Acid 85%	13.5
	468.0

The essential components in this composition are as follows:—

	Parts by Weight
(A) Tetrafluoroethylene Polymer	85
(B) Organopolysiloxane Resins	15
(C) Surfactants—(Anionic	11.0
(Non-ionic	27.3
(D) Polybasic Oxy-acids—(CrO_3	13.5
(H_3PO_4	11.5
(E) Pigment	50

There are 17.7 parts of the organopolysiloxane resin per 100 parts of the perfluorocarbon polymer. There are 45 parts of total surfactant per 100 parts of the perfluorocarbon polymer of which surfactant mixture about 13 parts are the anionic surfactant.

There are 25 parts of the oxy-acids per 100 parts total weight of the perfluorocarbon polymer and the organopolysiloxane resin.

There are 50 parts of pigment per 100 parts total weight of the perfluorocarbon polymer and the organopolysiloxane resin.

The ingredients of the first portion are mixed and then ball mill ground for about 72 hours to disperse the pigment. The ingredients of the second portion are mixed to provide an aqueous dispersion having the solution of organopolysiloxane resins as the dispersed phase. DC-801 and DC-803 are heat-convertible methyl-phenylpolysiloxane resins in solution in xylol. DC-801 at 60% in xylol is characterized by a viscosity at 25°C in the range of D to L Gardner-Holdt scale and DC-803 at 50% in xylol is characterized by a viscosity at 25°C in the range of D to H. Then the remaining portions are added in order.

This coating composition is applied as a single thick coat of about 1 mil to the interior surface of an aluminum ice cube tray and the applied coating is cured by heating for about 6 minutes at 725°F. The resulting coating is hard, abrasion-resistant, and adherent to the metal. Another ice cube tray is coated with an ordinary commercially available "Teflon" (trade mark) TFE perfluorocarbon resin primer at about 0.3 mil and topcoat of about 0.7 mil, and cured under the same conditions. The resulting composite coating is relatively soft, is easily abraded or scratched, and is weakly anchored to the substrate. The combination of primer and topcoat provides about the same coating thickness as the single coat of the invention composition. The two trays are filled with water and placed in a freezer to produce ice. Release properties relative to ice are satisfactory, the Example 1 coating being rated only slightly less effective than the comparative coating.

The composition of Example 1 is applied as a single coat of about 1 mil to the baking surfaces of an electric grill for frying pancakes and baking waffles and over a portion of the coated area is applied an ordinary clear coating of tetrafluoroethylene polymer composition. The coatings are cured and fused by heating for about 20 minutes at 725°F. A comparative grill is coated with a two-coat system of ordinary "Teflon" primer and clear "Teflon" topcoat, and over a portion of the coated area is applied a coat of the composition of Example 1. The coatings on the comparative grill are cured under the same conditions. The coated area having solely the cured coating of Example 1 exhibits the same characteristics as indicated for the coated ice cube tray, and the coated area having solely the comparative combination primer-topcoat finish exhibits the same deficiencies noted for the ice cube tray similarly coated. An improved bondage is observed at the interface between the invention finish and the comparative clear tetrafluoroethylene polymer finish.

Use of the coated grills for frying pancake batter and baking waffles reveals no significant difference in the release properties of the respective coated areas in reference to releasing the baked products from the grills. A particular advantage of the area coated with the Example 1 composition is that it is harder and less easily marked when abraded with a metal spatula or pancake turner in comparison with the area coated with the ordinary perfluorocarbon polymer finish.

EXAMPLE 2

	Parts by Weight		
	A	*B*	*C*
First Portion			
Toluol	12.7	20.0	41.5

"Triton" X-100 Non-ionic Surfactant	3.0	4.6	9.5
DC-803 Organopolysiloxane Resin Solution—50% in Xylol	7.3	11.4	24.0
TiO_2 Pigment	32.0	50.0	103.0
Second Portion			
DC-801 Organopolysiloxane Resin solution—60% in Xylol	7.4	6.3	6.7
DC-803 Organopolysiloxane Resin Solution——50% in Xylol	8.8	7.6	8.0
"Triton" X-100 Non-ionic Surfactant	10.0	10.0	—
Xylol	40.0	20.0	—
Aqueous Sodium Lauryl Sulfate Solution — 23%	47.7	46.9	47.0
Water	23.1	43.2	48.3
Third Portion			
Aqueous Suspensoid of Tetrafluoroethylene Polymer — 60% Plus 3 Parts of Sodium Lauryl Sulfate per 100 Parts of Polymer	145	145	133
Fourth Portion			
Chromic Acid Flake 99.5+% CrO_3	24.0	24.0	24.0
Orthophosphoric Acid—85%	19.0	19.0	19.0
Water	70.0	104.0	142.0
	450.0	512.0	606.0

The composition ratios are:

	2A	2B	2C
Tetrafluoroethylene Polymer	87.0	87.0	80.0
Organopolysiloxane Resin	12.5	13.3	20.0
Surfactant	26.6	27.0	22.7
Oxy-acid	40	40	40
Pigment	32	50	100

These respective compositions are prepared by the same technique as described for Example 1. The fourth portion is withheld and blended with the combined preceding portions immediately prior to application.

About one-half the surface of an aluminum griddle is prime-coated with an ordinary tertafluoroethylene polymer primer 850-204 at about 0.4 mil and baked for 20 minutes at 715°F. To this primed surface is applied an ordinary tetrafluoroethylene polymer topcoat 851-221 at about 0.8 mil, over the remaining half the surface with about 1 inch overlap of the primed surface, the composition of Example 2C is applied at about 1.2 mils. The topcoats are flash-dried for 15 minutes at 170°F and then cured by heating for 25 minutes at 750°F.

Eggs are fried in bacon grease using the coated griddle. The area coated with the Example 2C composition exhibits inferior release properties and is softened by the hot grease and easily separated from the metal after about one month of daily use, indicating a diminution of the tetrafluoroethylene copolymer properties to the coating in comparison with the ordinary tertafluoroethylene polymer comparative coating. However, the invention composition is harder and more abrasion-resistant than the comparative coating.

The desirable heat resistance, chemical resistance, and release properties characteristic of tetrafluoroethylene polymer are restored to the finish when the compositions of Examples 2A and 2B are used respectively in place of 2C. The cured compositions of 2A and 2B exhibit significant improvement over the ordinary tetrafluoroethylene polymer coatings in reference to hardness and abrasion resistance.

Aluminum and steel panels are primed with the Example 2C composition at about 1 mil dry thickness. One set of panels is cured by air-drying overnight and a second set is cured by heating for 20 minutes at 715°F. Ordinary baking finishes formulated respectively with epoxypolyether resins, urea-formaldehyde resins, melamine-formaldehyde resins, drying oil-modified alkyd resins, and vinyl resins are applied at a coating thickness of about 1 mil over the air-dry primer and fused primer, and then the respective topcoats are baked according to their ordinary baking schedules. The cured finishes adhere well to both the air-dried primer and the fused primer of Example 2C. Use of this and like compositions of this invention provide an opportunity of preparing composite finishes which include a perfluorocarbon polymer layer and which exhibit intercoat adhesion between this layer and another layer of organic film-forming material which ordinarily does not adhere well to ordinary tetrafluoroethylene polymer coatings.

EXAMPLE 3

	Parts by Weight
First Portion	
Toluol	40.0
"Triton" X-100 Non-ionic Surfactant	9.0
DC-803 Organopolysiloxane Resin Solution, 50% in Xylol	23.2
Ti_2O Pigment	100.0
Second Portion	
DC-801 Organopolysiloxane Resin Solution, 60% in Xylol	7.0
DC-803 Organopolysiloxane Resin Solution, 50% in Xylol	8.4
Aqueous Sodium Lauryl Sulfate Solution, 23%	32.1
Water	53.3

Third Portion

Aqueous Suspenoid of Tetrafluoroethylene Polymer—60% Plus 3 Parts of Sodium Lauryl Sulfate per 100 Parts of Polymer	67.0
Aqueous Suspensoid of Hexafluoropropylene / Tetrafluoroethylene Interpolymer — 60% Plus 6 Parts of "Triton" X-100 per 100 Parts of Interpolymer	67.0
Fourth Portion	
Chromic Acid	25.8
Orthophosphoric Acid—85%	25.8
Water	78.4
	537.0

The composition is prepared by the same technique as described for Example 1. The essential difference between this composition and the preceding formulations is that the perfluorocarbon polymer component consists of equal proportions of hexafluoropropylene-tetrafluoroethylene interpolymer and tetrafluoroethylene homopolymer. The interpolymer is commercially available as having a content of about 15% to 20% of copolymerized hexafluoropropylene.

The ratios in this composition are:

Perfluorocarbon Polymer	80
Organopolysiloxane Resin	20
Surfactant	19.8
Oxy-acid	47.8
Pigment	100

This coating is applied to a series of aluminum and steel panels at several film thicknesses ranging from 0.5 to 4 mils per dry coat. One series of coated panels is permitted to air-dry. A second series of the primed panels is permitted to air-dry for about 6 minutes, then coated with an ordinary tetrafluoroethylene polymer topcoat composition at about 1 mil thickness, and then cured by baking for 10 minutes at 750°F. A third series of the primed panels is heated for 6 minutes at 750°F, then coated with the ordinary tetrafluoroethylene polymer coating composition and heated for 10 minutes at 750°F.

The adhesion of the air-dried primer coat to the respective substrates is rated in the range of good to very good. The adhesion of the primer cured at 750°F is rated very good. The composite finish of the Example 3 composition as a primer and a topcoat of the ordinary tetrafluoroethylene polymer composition is rated very good for adhesion to the substrates and rated good for intercoat adhesion when the primer is air-dried and the composite finish is cured as a unit. The composite finish having the topcoat applied over the fused primer exhibits a lesser degree of intercoat adhesion. These finishes and combination finishes provide high film builds which cannot be accompished with one and two coats of ordinary tetrafluoroethylene polymer finishes.

EXAMPLE 4

This composition is prepared identical with that of Example 3 except that the third portion consists of 125 parts of the aqueous suspensoid of the perfluorocarbon interpolymer and the suspensoid of the tetrafluoroethylene polymer is omitted.

This composition is applied at film thicknesses ranging up to 3 mils in a single coat to aluminium and steel panels. After two hours air drying, the dry coatings exhibit fair to good adhesion to the substrates. After curing for 20 minutes at 650°F the coatings exhibit very good adhesion to the substrates and very good intercoat between the Example 4 composition as the primer and an ordinary topcoat formulated with the perfluorccarbon interpolymer.

EXAMPLE 5

	Parts by Weight
First Portion	
Toluol	34.2
"Triton" X-100 Non-ionic Surfactant	7.8
DC-803 Organopolysiloxane Resin Solution, 50% in Xylol	19.0
TiO_2 Pigment	85.0
Second Portion	
DC-801 Organopolysiloxane Resin Solution, 60% in Xylol	12.2
DC-803 Organopolysiloxane Resin Solution, 50% in Xylol	14.6
SR-82 Organopolysiloxane Resin Solution, 60% in Toluol	40.5
Aqueous Sodium Lauryl Sulfate Solution, 23% in Water	69.7
"Triton" X-100 Non-ionic Surfactant	24.5
Toluol	63.7
Water	136.3
Third Portion	
Aqueous Suspensoid of Tertafluoroethylene Polymer — 60% Plus 3 Parts of Sodium Lauryl Sulfate per 100 Parts of the polymer	323.0
Fourth Portion	
Chromic Acid	51.0
Orthophosphoric Acid—85%	51.0
Water	117.5
	1050.0

The ratios in this composition are as follows:

Perfluorocarbon Polymer	194
Organopolysiloxane Resin	48.4
Surfactants	54.2
Oxy-acids	94
Pigment	85

This composition is prepared by the same technique as described for Example 1.

The composition of the fourth portion is suoh that one a volume basis, one quart of the fourth portion is blended with one gallon

of the combined first three portions to complete the final composition. The final composition has a useful pot-life of about 6 hours, pot-life to coagulation being about 36 hours.

At curing temperatures below about 650°F, the cure of the film depends on a time-temperature reaction between the reactive organopolysiloxane resin and the oxy-acids, i.e., chromic and phosphoric acids. The hardness and hydrophobic properties of the applied coating increase as the time and temperature of the cure is increased up to about 750°F. The coating air-dries satisfactorily at ambient temperatures, e.g., 77°F. At drying temperatures in the range of 70°F to 125°F, hardness, adhesion and hydrophobic properties are improved by exposure of the coating to sunlight or to ultraviolet light.

composite finishes of ordinary topcoats based on tetrafluoroethylene polymer applied over the Example 5 composition as a primer unfused, and the composite finish cured at fusion temperature, exhibit good adhesion of the topcoat. Intercoat adhesion is inferior when the primer is initially fused and then topcoated with an ordinary tetrafluoroethylene polymer coating.

EXAMPLE 6

	Parts by Weight
First Portion	
Carbon Black Pigment	7.7
Aluminum Silicate Extended Pigment	1.5
Water	15.6
Anionic Surfactant—Sodium Sulfonate of Naphthalene/Formaldehyde Condensate	0.8
Second Portion	
DC-803 Organopolysiloxane Resin Solution, 50% in Xylol	40.0
Toluol	86.8
"Triton" X-100 Non-ionic Surfactant	20.0
Water	100.0
Third Portion	
Perfluorocarbon Interpolymer Suspensoid, 55%	254.4
Tetrafluoroethylene Polymer Suspensoid, 60%	233.2
Fourth Portion	
Chromic Acid	160.0
Orthophosphoric Acid	40.0
Water	40.0
	1000.0

The perfluorocarbon interpolymer suspensoid is 55% interpolymer in water commercially available as "Teflon" TE-9500 perfluorocarbon polymer suspensoid containing about 6 parts of "Triton" X-100 and 0.75 part of fluorocarbon surfactant per 100 parts of the interpolymer. The tetrafluoroethylene polymer suspensoid is at 60% concentration prepared by electrodecantation from the commercially available 34% suspensoid, and having a content of 3 parts of sodium lauryl sulfate per 100 parts of polymer in the aqueous medium.

The first portion is pebble mill ground for 30,000 cycles. The second portion is emulsified, blended with the first portion, and the third portion blended therewith. The fourth portion is blended with the premixed first three portions immediately prior to application.

The ratios of the components are:

Perfluorocarbon Polymer	280.0
Organopolysiloxane Resin	20.0
Surfactant	34.5
Oxy-acids	194.0
Pigment	9.2

This composition is sprayed on steel panels at a dry film thickness of about 1 mil and cured by heating for 15 minutes at 750°F. The resulting cured finish is rated as good in reference to adhesion, cohesion, hardness and flexibility and very good in general appearance, exhibiting significant improvement over an ordinary tetrafluoroethylene polymer primer applied at about 0.5 mil thickness.

Example 6A is prepared identical with that of Example 6 except that the orthophosphoric acid is omitted. The properties of the resulting finish cured under the same conditions are comparable with those of the Example 6 composition except that adhesion is rated second best, but better than that of the comparative tertafluoroethylene polymer primer.

Example 6B is likewise prepared identical with that of Example 6 except sulfuric acid replaces the orthophosphoric acid. The cured finish from this composition is rated comparable with that from Example 6A, indicating that the dibasic sulfuric acid is not as effective as the tribasic phosphoric acid in combination with the chromic acid.

Example 6C is prepared identical with Example 6 except that the chromic acid is omitted. The cured finish from this composition exhibits good adhesion, but in the absence of the chromic acid, only minor improvement in cohesion, hardness, and flexibility is registered over the ordinary tetrafluoroethylene polymer primer.

Example 6D is prepared identical with the composition of Example 6 except that the chromic acid content is 10 parts. The cured finish from this composition exhibits good adhesion and significant improvement over the Example 6C cured finished in reference to hardness, cohesion and flexibility.

WHAT WE CLAIM IS:—

1. A water-dilutable aqueous dispersion coating composition consisting essentially of:

(A) colloid particles of at least one perfluorocarbon polymer, said polymer being

tetrafluoroethylene polymer or hexafluoropropylene/tetrafluoroethylene interpolymer, dispersed in an aqueous continuous phase.

(B) a solution of a heat-convertible (as herein defined) organo-polysiloxane resin containing structural units of the formula:

$$-\overset{\displaystyle R}{\underset{\displaystyle R'}{\overset{|}{\underset{|}{Si}}}}-O-$$

in which R and R′, which may be the same or different (and which may vary from one structural unit to another), are monovalent hydrocarbon radicals in a water-immiscible organic solvent therefore as a dispersed phase,

(C) a sufficient quantity of one or more water-soluble anionic surfactants to maintain the stability of the dispersion of the perfluorocarbon polymer and the solution of organo-polysiloxane in the continuous aqueous phase, and

(D) chromic acid.

2. A coating composition according to claim 1, which also includes one or more non-ionic water-soluble surfactants.

3. A coating composition according to claim 1 or 2, which also includes a polybasic oxy-acid of phosphorus or sulphur.

4. A coating composition according to any of claims 1 to 3 in which from 50% to 100% of the hydrocarbon radicals in the polysiloxane are methyl and phenyl radicals.

5. A coating composition according to claim 4, in which the ratio of methyl to phenyl radicals in the polysiloxane is from 0.5:1 to 2:1.

6. A coating composition according to any of claims 1 to 5 in which the organo-polysiloxane is present in the proportion of from 3 to 100 parts per 100 parts by weight of the perfluorocarbon polymer.

7. A coating composition according to any of claims 1 to 6, containing a mixture of chromic acid and orthophosphoric acid, the proportion of chromic acid being at least 5 parts per 100 parts total weight of the perfluorocarbon polymer and the organo-polysiloxane resin and the total proportion of chromic acid and orthophosphoric acid being up to 200 parts on said basis.

8. A coating composition according to claim 7, in which the oxy-acid mixture consists of 50 to 150 parts of orthophosphoric acid per 100 parts of chromic acid, the total proportion of the two oxy-acids being up to 100 parts on the indicated basis.

9. A coating composition according to any of claims 1 to 8, containing from 3 to 50 parts of surfactant per 100 parts by weight of perfluorocarbon polymer.

10. A coating composition according to any of claims 1 to 9, in which a mixture of a sodium alkyl sulphate and an alkylphenoxypolyethanoxyethanol is used as the surfactant.

11. A composition according to any of claims 1 to 10, which also contains up to 500 parts of pigment per 100 parts total weight of the perfluorocarbon polymer and the organopolysiloxane resin.

12. A composition according to claim 11, containing from 10 to 150 parts by weight of pigment on the indicated basis.

13. A coating composition according to claim 1 in which the constituents are present in the following proportions:

	Parts by Weight
(A) Perfluorocarbon Polymer	100
(B) Organopolysiloxane Resin having structural units of the formula: $-\overset{\displaystyle R}{\underset{\displaystyle R'}{\overset{|}{\underset{|}{Si}}}}-O-$ in which R and R′, which may be the same or diferent (and which may vary from one structural unit to another) are monovalent hydrocarbon radicals, from 50% to 100% of which one are methyl and phenyl radicals, the ratio of the methyl to phenyl radicals being from 0.5:1 to 2:1	10 to 35
(C) Mixed Surfactant:	
sodium alkyl sulphate	5 to 20
alkylphenoxypolethanoxyethanol	5 to 30
(D) Chromic acid and, if desired, polybasic oxy-acid of phosphorous or sulphur	20 to 65

the proportion for (D) and (E) being based on 100 parts total weight of (A) plus (B).

14. A composition according to any of claims 1 to 13, in which a mixture of 5 to 90 parts by weight of tetrafluoroethylene polymer and 95 to 10 parts by weight of hexafluoroethylene/tetrafluoroethylene interpolymer is used as the perfluorocarbon polymer.

15. As an article of manufacture, a heat-resistant substrate having, as a finish thereon, at least one dry coat of the composition claimed in any of claims 1 to 14.

16. As an article of manufacture, a heat-resistant substrate having, as a finish thereon, at least one fused dry coat of the composition claimed in any of claims 1 to 14.

17. As an article of manufacture, a heat-resistant substrate having a dry coat of the composition claimed in any of claims 1 to 14 as a primer coat, and superimposed there-

on, at least one dry coat of a coating composition comprising a heat-convertible resin as the essential organic film-forming material.

18. A method of preparing a coating composition which comprises mixing a solution of a heat-convertible as herein defined organopolysiloxane resin in a water-immiscible solvent therefor with water in the presence of a surfactant, thereby forming a dispersion of said solution of resin as the dispersed phase in a continuous aqueous phase, blending the resulting aqueous dispersion with an aqueous suspensoid of colloidal particles of a perfluorocarbon polymer, said polymer being tetrafluoroethylene polymer or hexafluoropropylene/tetrafluoroethylene interpolymer, in the presence of an anionic surfactant, and thereafter blending chromic acid and, if desired, a polybasic oxy-acid of phosphorus or sulphur, the essential components being in the proportion of:

	Parts by Weight
(A) Perfluorocarbon Polymer	100
(B) Organopolysiloxane Resin	3 to 100
(C) Surfactant, including at least 2 parts of anionic species	3 to 50
(D) Chromic acid, and if present, other oxy-acid	5 to 200

the proportion of oxy-acid being based on 100 parts total weight of (A) plus (B).

19. A method according to claim 18 which includes the further step of dispersing pigment in a liquid medium in the presence of a surfactant soluble in the liquid medium and blending the resulting dispersed pigment with the aqueous dispersion of the solution of said organopolysiloxane resin and the aqueous suspensoid of said perfluorocarbon polymer, the proportion of pigment being up to 500 parts by weight per 100 parts total weight of said perfluorocarbon polymer and said organopolysiloxane resin.

20. A method according to claim 19, in which said pigment is dispersed in a solution of said organopolysiloxane resin in a water-immiscible organic solvent therefor and containing a soluble surfactant.

21. A water-dilutable aqueous dispersion coating composition according to claim 1 substantially as herein described in any of the Examples.

22. A method of preparing a coating composition according to Claim 18 substantially as herein described in any of the Examples.

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